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Rate constant for thermal unimolecular reactions in intermediate collision cases

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Abstract. A procedure is developed to obtain converging bounds to the rate, at all pressures, of a thermal unimolecular reaction for which the corresponding relaxation matrix is represented as a linear combination of a weak-collision and a strong-collision rate matrix. A pair of bounds to the rate is given in a closed form in terms of the matrix elements. The method is illustrated by a numerical example.

1. Introduction

The rate constant, γ_0, is defined to be the smallest eigenvalue of the matrix $(\mathbf{L}+\mathbf{D})$ where $\mathbf{L}$ is a relaxation matrix and $\mathbf{D}$ is a non-negative diagonal matrix of decay rates, representing a thermal unimolecular reaction. In two preceding papers (Vatsya and Pritchard 1981a, b) we studied the two limiting cases: the weak collision (Vatsya and Pritchard 1981b) and the strong collision (Vatsya and Pritchard 1981a), characterised by $\mathbf{L}=\mathbf{B}$ and $\mathbf{L}=\mathbf{A}$ respectively, where $\mathbf{B}$ is a real, symmetric tridiagonal matrix and $\mathbf{A}=\mu(1-p_0)$ with μ being a constant, proportional to the pressure. Here p_0 is the projection $S_0(S_0,\ )$ where $(\ ,\ )$ denotes the scalar product and S_0 is a normalised vector with ith element $\tilde{n}_i^{1/2}$ where $\tilde{n}_i$ is the Boltzmann equilibrium population of the state i. Thus the i, jth element of $\mathbf{A}$ is

$$\mu(\delta_{ij}-\tilde{n}_i^{1/2}\tilde{n}_j^{1/2}).$$

Also the lowest eigenvalue, zero, of $\mathbf{B}$ is simple with the corresponding eigenvector being S_0 (Pritchard and Lakshmi 1979) and the next eigenvalue is not less than μ. In this paper we consider the case of 'intermediate collision' reactions represented by

$$\mathbf{L}=[(1-\xi)\mu(1-p_0)+\xi\mathbf{B}] \qquad 0\leqslant\xi\leqslant 1.$$

These matrices tend to exhibit severe bottleneck properties (Vatsya and Pritchard 1981b) in the sense that γ_0 is insensitive to variations in the elements $\mathbf{B}_{ij}$ of $\mathbf{B}$ over quite wide ranges, but outside certain limits γ_0 varies rapidly with variations of certain of the $\mathbf{B}_{ij}$. It is impractical to explore these effects by numerical solutions of the eigenvalue problem. In this paper we develop a procedure to produce sequences converging to γ_0 from above and below. These approximations are expressed explicitly in terms of $\mathbf{B}_{ij}$, which will greatly facilitate the task of correlating the behaviour of γ_0 with variations of these elements.

2. Preliminaries

In this section we consider the problem of approximating the lowest eigenvalue σ_0 of a real symmetric matrix $[\mu(1-p_0)+C]$ with $C \geqslant 0$. It is clear that $\sigma_0 \geqslant 0$. It will be assumed that $\sigma_0 < \mu$, and the trivial case $\sigma_0 = 0$ will be excluded.

Let ψ_0 be an eigenvector of $[\mu(1-p_0)+C]$ corresponding to the eigenvalue σ_0. The eigenvalue equation reads

$$(\mu + C - \sigma_0)\psi_0 = \mu S_0(S_0, \psi_0) \tag{1}$$

and $(S_0, \psi_0) \neq 0$, otherwise $\sigma_0 \geqslant \mu$ or $\psi_0 = 0$. It now follows that the eigenspace corresponding to σ_0 is spanned by the single vector $(\mu + C - \sigma_0)^{-1} S_0$; hence σ_0 is a simple eigenvalue. We define functions $\phi(x)$, $\bar{\phi}(x)$ and $\chi(x)$ on $(-\infty, \mu)$ as

$$\phi(x) = \mu(S_0, (\mu + C - x)^{-1} S_0) \tag{2a}$$

$$\begin{aligned}\bar{\phi}(x) &= \mu(S_0, (\mu + C - x)^{-1} C S_0)\\ &= \mu(\bar{S}_0, (\mu + C - x)^{-1} \bar{S}_0)\\ &= \mu - (\mu - x)\phi(x)\end{aligned} \tag{2b}$$

$$\begin{aligned}\chi(x) &= (\bar{S}_0, [1 + (\mu - x)^{-1} C^{1/2}(1-p_0)C^{1/2}]^{-1} \bar{S}_0)\\ &= \frac{(\mu - x)(\bar{S}_0, (\mu + C - x)^{-1}\bar{S}_0)}{1 - (\bar{S}_0, (\mu + C - x)^{-1}\bar{S}_0)}\\ &= \frac{(\mu - x)\bar{\phi}(x)}{\mu - \bar{\phi}(x)}\\ &= \frac{\bar{\phi}(x)}{\phi(x)}\end{aligned} \tag{2c}$$

where $\bar{S}_0 = C^{1/2} S_0$. Since $C \geqslant 0$, $C^{1/2}$ is well defined. In lemma 1 we show that these functions determine σ_0 uniquely.

Lemma 1. Let σ_0, $\phi(x)$, $\bar{\phi}(x)$ and $\chi(x)$ be as above. Then σ_0 is the unique zero of $(\phi(x) - 1)$, and the unique fixed point of $\bar{\phi}(x)$ and $\chi(x)$ in $(-\infty, \mu)$.

Proof. The fact that $\phi(\sigma_0) = 1$ follows from (1) using the invertibility of $(\mu + C - \sigma_0)$ and $(S_0, \psi_0) \neq 0$ for $\sigma_0 < \mu$.

It is clear from (2a) that $\phi(-\infty) = 0$, $\phi(x) \geqslant 0$ for x in $(-\infty, \mu)$ and

$$\phi'(x) = \mathrm{d}\phi(x)/\mathrm{d}x = \mu(S_0, (\mu + C - x)^{-2} S_0) \geqslant 0.$$

In fact $\phi'(x) \neq 0$ since the equality implies that $S_0 = 0$. Thus $\phi(x)$ is a strictly increasing function. Therefore $\phi(x) = 1$ can have at most one solution.

It is straightforward to check that $\phi(x) = 1$ if and only if $\bar{\phi}(x) = x$ and $\chi(x) = x$.

We have already observed that $\phi'(x) > 0$. By the same argument we have that $\phi''(x) > 0$. Furthermore, $\bar{\phi}'(x)$ and $\bar{\phi}''(x)$ are positive and $\chi'(x)$ and $\chi''(x)$ are negative unless $\bar{S}_0 = 0$. But $C^{1/2} S_0 = 0$ implies that $[\mu(1-p_0)+C]S_0 = 0$, i.e. $\sigma_0 = 0$; thus this possibility is excluded. We state this result as follows.

Corollary 1. The functions $\phi(x)$, $\bar{\phi}(x)$ are positive, increasing and convex on $(-\infty, \mu)$ and $\chi(x)$ is positive, decreasing and concave there.

In view of the results of lemma 1 and corollary 1, the iterative method may be used to obtain lower and upper bounds to σ_0 by way of approximating the fixed points of $\bar{\phi}(x)$ and $\chi(x)$. Also Newton's method may be used to obtain both the bounds by way of solving $\phi(x)=1$, $\bar{\phi}(x)=x$ and $\chi(x)=x$. We state these results in theorems 1 and 2.

Theorem 1. (The iterative method.)

(i) Let $x_0 \leqslant \sigma_0$ and $x_{m+1}=\bar{\phi}(x_m)$, $m=0,1,2,\ldots$; then $x_m \uparrow \sigma_0$.

(ii) Let $\mu > x_0 \geqslant \sigma_0$ and $x_{m+1}=\bar{\phi}(x_m)$, $m=0,1,2,\ldots$; then $x_m \downarrow \sigma_0$.

(iii) Let $x_{m+1}=\chi(x_m)$, $m=0,1,2,\ldots$, with $x_0<\mu$ such that $0 \leqslant x_m < \mu$, $m>0$. Then $x_0 \leqslant \sigma_0$ implies that $x_{2m} \uparrow y_0 \leqslant \sigma_0 \leqslant y_1 \downarrow x_{2m+1}$. If $x_0 \geqslant \sigma_0$ then the bound properties are reversed.

Proof. For (i) and (ii) see Vatsya and Pritchard (1981a) and theorem 2 of Singh (1981). For (iii) see theorem 1 of Vatsya and Pritchard (1981b).

It may happen in theorem 1(iii), if $x_0<\sigma_0$ ($x_0>\sigma_0$), that $y_0<\sigma_0<y_1$ ($y_0>\sigma_0>y_1$). The sequences convergent to the fixed point of $\chi(x)$ may, however, be found by using the min–max method (Vatsya 1981). To be precise, let $x_0<\mu$, $\chi(x_0)=x_1<\mu$. It is obvious that $\bar{x}_0=\min(x_0,x_1)\leqslant\sigma_0\leqslant\max(x_0,x_1)=\bar{x}_1$. Pick some positive $\varepsilon<1$ and let $a_m=(1-\varepsilon)\bar{x}_{2m}+\varepsilon\bar{x}_{2m+1}$, $\bar{x}_{2m+2}=\max(\bar{x}_{2m}, \min(a_m,\chi(a_m)))$, $\bar{x}_{2m+3}=\min(\bar{x}_{2m+1}, \max(a_m,\chi(a_m)))$ for $m=0,1,2,\ldots$. Then $\bar{x}_{2m+1}\downarrow\sigma_0\uparrow\bar{x}_{2m}$.

Theorem 2 may be deduced by arguments similar to theorem 1. Therefore we state the results without proof.

Theorem 2. (The Newton method.)

(i) Let $x_{m+1}=x_m+(1-\phi(x_m))/\phi'(x_m)$, $m=0,1,2,\ldots$, with $x_0<\mu$ such that $x_1<\mu$; then $x_m\downarrow\sigma_0$.

(ii) Let $x_0\leqslant\sigma_0$ and $x_{m+1}=(\bar{\phi}(x_m)-x_m\bar{\phi}'(x_m))/(1-\bar{\phi}'(x_m))$, $m=0,1,2,\ldots$; then $x_m\uparrow\sigma_0$.

(iii) Let $x_{m+1}=(\chi(x_m)-x_m\chi'(x_m))/(1-\chi'(x_m))$, $m=0,1,2,\ldots$, with $x_0<\mu$ such that $x_1<\mu$; then $x_m\downarrow\sigma_0$.

The information required in theorems 1 and 2, as well as in the min–max method, in order to determine the sequences of bounds to σ_0, is covered by the functions $\phi(x)$, $\bar{\phi}(x)$, $\chi(x)$ and their derivatives for an arbitrary $x<\mu$. As is clear from equations (2a) to (2c), knowledge of $\phi(x)$ and $\phi'(x)$ is sufficient, which is determined by $\beta(x)=(\mu+C-x)^{-1}S_0$.

It is pertinent to remark that the condition $\sigma_0<\mu$ can be relaxed. It is obvious that σ_0 is less than or equal to the lowest eigenvalue of $(\mu+C)$. If σ_0 is not necessarily less than μ, then the above results on $\phi(x)$ are still true. Thus σ_0 can be approximated using theorem 2(i). However, since theorem 2(i) yields upper bounds to σ_0, it also provides a means to check if theorem 2(ii), (iii) are applicable to a particular problem. In the following, as above, we assume that $\sigma_0<\mu$; the modifications for the other case are straightforward as explained here.

3. Approximations to γ_0

The rate constant γ_0 is defined to be the smallest eigenvalue of the matrix $[(1-\xi)\mu(1-p_0)+\xi\mathbf{B}+\mathbf{D}]=\mu(1-p_0)+C$, where $C=\xi(\mathbf{B}-\mu+\mu p_0)+\mathbf{D}$, $0\leqslant\xi\leqslant1$. The cases $\xi=0$

and $\xi = 1$ represent the strong-collision and weak-collision cases, respectively. Here $\mathbf{D}$ is a non-negative diagonal matrix and $\mathbf{B}$ is a real, symmetric tridiagonal matrix. Further, the lowest eigenvalue zero of $\mathbf{B}$ is simple with the corresponding eigenvector S_0; the next eigenvalue is greater than or equal to μ.

Since an arbitrary vector $\psi \neq 0$ can be written as $\psi = \alpha S_0 + \bar{\psi}$ with some constant α and $(S_0, \bar{\psi}) = 0$, we have that

$$\frac{(\psi, C\psi)}{(\psi, \psi)} \geq \xi \frac{(\bar{\psi}, (\mathbf{B}-\mu)\bar{\psi})}{\alpha^2 + (\bar{\psi}, \bar{\psi})} \geq 0.$$

Thus $C \geq 0$ and we assume that $\gamma_0 < \mu$. Now, the results of § 2 are applicable and the problem has been reduced to determining $\beta(x)$ where

$$\begin{aligned}\beta(x) &= (\mu + C - x)^{-1} S_0 \\ &= (\mathbf{T} + \xi\mu p_0)^{-1} S_0 \\ &= \mathbf{T}^{-1}(1 + \xi\mu p_0 \mathbf{T}^{-1})^{-1} S_0 \\ &= \frac{\mathbf{T}^{-1} S_0}{1 + \xi\mu (S_0, \mathbf{T}^{-1} S_0)} \end{aligned} \tag{3}$$

whenever $\mathbf{T}^{-1} = (\mu + \xi\mathbf{B} - \xi\mu + \mathbf{D} - x)^{-1}$ is defined. However, $\mathbf{T}$ is non-invertible precisely for one value of x in $(-\infty, \mu)$ which we show in lemma 2 where we propose a remedy as well.

Lemma 2. The matrix $\mathbf{T}(x)$ has a zero eigenvalue if and only if $\phi(x) = \xi^{-1}$. At $x = \phi^{-1}(\xi^{-1})$, $\phi'(x) = (\bar{\theta}, \bar{\theta})/\mu\xi^2(S_0, \bar{\theta})^2$ with an arbitrary $\bar{\theta}$ such that $\mathbf{T}\bar{\theta} = 0$.

Proof. If there is a vector $\theta \neq 0$ such that $\mathbf{T}\theta = 0$, $x < \mu$, then as in lemma 1,

$$\theta = \xi\mu(\mu + C - x)^{-1} S_0 (S_0, \theta)$$

and $(S_0, \theta) \neq 0$. It is now clear that $\mathbf{T}\theta = 0$ implies that $\phi(x) = \xi^{-1}$. Conversely, if $\phi(x) = \xi^{-1}$, then the vector $(\mu + C - x)^{-1} S_0 \neq 0$ is easily seen to be an eigenvector of $\mathbf{T}$ with the corresponding eigenvalue being zero.

It is also clear that the zero eigenvalue is simple, i.e. if $\mathbf{T}\bar{\theta} = 0$ then $\bar{\theta} = k(\mu + C - x)^{-1} S_0$ with some $k \neq 0$. In fact $k = \mu(S_0, \bar{\theta})/\phi(x) = \xi\mu(S_0, \bar{\theta})$. Consequently

$$\begin{aligned}\phi'(x) &= \mu(S_0, (\mu + C - x)^{-2} S_0) \\ &= \frac{(\bar{\theta}, \bar{\theta})}{\xi^2 \mu (S_0, \bar{\theta})^2}.\end{aligned}$$

Thus if $\mathbf{T}^{-1}$ does not exist then $\phi(x)$ and $\phi'(x)$ are as given in lemma 2 and if it does, the same functions are obtained by using (3).

The matrix $\mathbf{T}$ is an irreducible real symmetric matrix of order n. Hence all of its eigenvalues are simple. Let α be a vector with components α_i, $i = 0, 1, \ldots, (n-1)$ such that $\alpha_0 = 1$, $\alpha_1 = -\mathbf{T}_{00}/\mathbf{T}_{01}$, $\alpha_{i+1} = -(\mathbf{T}_{ii-1}\alpha_{i-1} + \mathbf{T}_{ii}\alpha_i)/\mathbf{T}_{ii+1}$ for $i = 1, 2, \ldots, (n-2)$. Since $\mathbf{T}$ is irreducible, none of the elements adjacent to the diagonal in $\mathbf{T}$ is zero. Now, let $\alpha_n = -(\mathbf{T}_{n-1\, n-2}\alpha_{n-2} + \mathbf{T}_{n-1\, n-1}\alpha_{n-1})$; it is straightforward to check that $\mathbf{T}$ has a zero eigenvalue if and only if $\alpha_n = 0$ (see also Pritchard and Vatsya (1982), lemma 6). Thus if $\alpha_n = 0$ then $\phi(x)$ and $\phi'(x)$ are determined by lemma 2; if $\alpha_n \neq 0$ then $\mathbf{T}$

is invertible. In the latter case, let $f = \mathbf{T}^{-1}g$ with an arbitrary n-vector g. As a corollary of theorem 2 of Pritchard and Vatsya (1982), we have that

$$f_i = -\sum_{j=i}^{n-1}\sum_{k=0}^{j}\frac{\alpha_i\alpha_k g_k}{\alpha_j\alpha_{j+1}T_{j\,j+1}} \qquad i=0,1,\ldots,(n-1) \tag{4}$$

where $\mathbf{T}_{n-1\,n} = \mathbf{T}_{n\,n-1} = 1$.

It is pertinent to remark here that the above result may be directly obtained relatively easily following the same steps. Another, even more explicit form of f is given by equation (12) of Pritchard and Vatsya (1982):

$$f_i = -\sum_{j=i}^{n-1}\sum_{k=0}^{j}\frac{P_i(0)P_k(0)}{P_j(0)P_{j+1}(0)}\prod_{l=i}^{j-1}\mathbf{T}_{l\,l+1}\prod_{m=k}^{j-1}\mathbf{T}_{m+1\,m}g_k \qquad i=0,1,\ldots,(n-1) \tag{5}$$

where $P_j(\lambda)$ are the Jacobi polynomials given by

$$P_0(\lambda)=1 \qquad P_1(\lambda)=\lambda-\mathbf{T}_{00} \qquad P_{k+1}(\lambda)=(\lambda-\mathbf{T}_{kk})P_k(\lambda)-\mathbf{T}^2_{k-1\,k}P_{k-1}(\lambda)$$
$$k=1,2,\ldots,(n-1).$$

From ($2a$) and (3) it follows for $x \neq \phi^{-1}(\xi^{-1})$, that

$$\phi(x) = N(x)/(1+\xi N(x))$$

where $N(x) = \mu(S_0, (\mu + \xi\mathbf{B} - \xi\mu + \mathbf{D} - x)^{-1}S_0)$. Using (5) this reduces to

$$\begin{aligned} N(x) &= -\mu\sum_{i=0}^{n-1}\sum_{j=i}^{n-1}\sum_{k=0}^{j}\frac{\tilde{n}_i^{1/2}P_i(0)P_k(0)\tilde{n}_k^{1/2}}{P_j(0)P_{j+1}(0)}\prod_{l=i}^{j-1}(\xi\mathbf{B}_{l\,l+1})\prod_{m=k}^{j-1}(\xi\mathbf{B}_{m+1\,m}) \\ &= -\mu\sum_{j=0}^{n-1}\frac{1}{\bar{P}_{j+1}(0)}\left(\sum_{i=0}^{j}\tilde{n}_i^{1/2}\prod_{l=i}^{j-1}(\xi\mathbf{B}_{l\,l+1}/\bar{P}_{l+1}(0))\right)^2. \end{aligned} \tag{6}$$

We have used the symmetry of $\mathbf{B}$, and $\bar{P}_{i+1}(0) = P_{i+1}(0)/P_i(0)$, $i = 0, 1, \ldots, n-1$, are given by

$$\bar{P}_1(0) = x - (1-\xi)\mu - \xi\mathbf{B}_{00} - \mathbf{D}_{00}$$
$$\bar{P}_{i+1}(0) = [x - (1-\xi)\mu - \xi\mathbf{B}_{ii} - \mathbf{D}_{ii}] - \xi^2\mathbf{B}^2_{i-1\,i}/\bar{P}_i(0).$$

If γ_0 is small in comparison with the other eigenvalues, the lower bound $\bar{\phi}(0)$ and the upper bound $\chi(0)$ are expected to be quite close. Thus the rate constant γ_0 may be approximated satisfactorily by using the inequality

$$\begin{aligned} \bar{\phi}(0) &= \mu(1-\phi(0)) = \mu\frac{1-(1-\xi)N(0)}{1+\xi N(0)} \\ &\leq \gamma_0 \\ &\leq \chi(0) = \frac{\bar{\phi}(0)}{\phi(0)} = \mu\frac{1-(1-\xi)N(0)}{N(0)}. \end{aligned}$$

In cases where $\bar{\phi}(0)$ and $\chi(0)$ are not close enough, further iterations may be necessary to obtain the degree of accuracy desired.

4. Numerical illustration

This method was implemented for the model calculation on the thermal dissociation of CO_2 at 4000 K which was described by Vatsya and Pritchard (1981b); the value of μ was taken to be $(\lambda_1 - \varepsilon)$ where λ_1 is the smallest non-zero eigenvalue of $\mathbf{B}$ and ε was of the order of $10^{-5}\lambda_1$. Upper and lower bounds, as given by (7), were calculated for $\xi = 0$, 0.25, 0.5, 0.75 and 1.0 and were found to be indistinguishable to at least five significant places for the whole range of pressures from 1 Torr to 10^9 Torr. The method is quite efficient, taking less than ten seconds of computing time in a contemporary mainframe computer for 27 values of pressure and all values of ξ. Only the results for four values of ξ are shown in figure 1, as the curve for $\xi = 0.75$ lies very close to the weak-collision curve, i.e. $\xi = 1$. The strong-collision curve lies below the weak-collision curve, because μ is close to the smallest eigenvalue of $\mathbf{B}$; therefore the relaxation described by $\mu(1 - p_0)$ is rather slower than that described by $\mathbf{B}$.

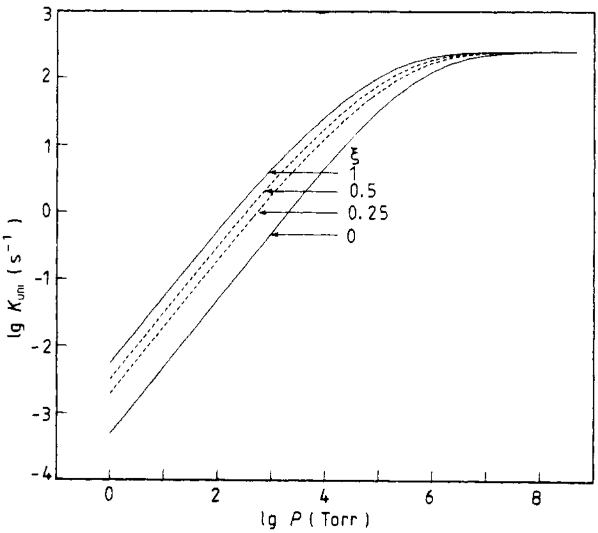

Figure 1. Model calculation for the fall-off in the dissociation of CO_2 at 4000 K, using a relaxation matrix of the form $[(1-\xi)\mu(1-p_0) + \xi\mathbf{B}]$.

The present method is superior to the one given earlier (Vatsya and Pritchard 1981b) not only in accuracy but also in speed and simplicity. Further, (6) shows the dependence of $N(x)$, and hence that of the approximations to γ_0, on $\mathbf{B}_{ij}$ and ξ quite explicitly, making the method suitable to explore this dependence.

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References

Pritchard H O and Lakshmi A 1979 *Can. J. Chem.* **57** 2793
Pritchard H O and Vatsya S R 1982 *J. Chem. Phys.* **76** 1024
Singh S R 1981 *J. Math. Phys.* **22** 893
Vatsya S R 1981 *J. Math. Phys.* **22** 2977
Vatsya S R and Pritchard H O 1981a *Can. J. Chem.* **59** 772
—— 1981b *Proc. R. Soc.* A **375** 409